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(12) United States Patent
Hebsur**(10) Patent No.: US 6,288,000 B1**
(45) Date of Patent: Sep. 11, 2001**(54) PEST RESISTANT MOSI₂-BASED MATERIALS CONTAINING IN-SITU GROWN β -Si₃N₄ WHISKERS****(75) Inventor: Mohan G. Hebsur**, North Olmsted, OH (US)**(73) Assignee: Ohio Aerospace Institute**, Cleveland, OH (US)**(*) Notice:** Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.**(21) Appl. No.: 09/500,497****(22) Filed: Feb. 9, 2000****(51) Int. Cl.⁷ C04B 35/58; C04B 35/81****(52) U.S. Cl. 501/95.3; 501/95.2; 501/96.3****(58) Field of Search 501/95.2, 95.3, 501/97.4, 96.3; 264/683****(56) References Cited****U.S. PATENT DOCUMENTS**

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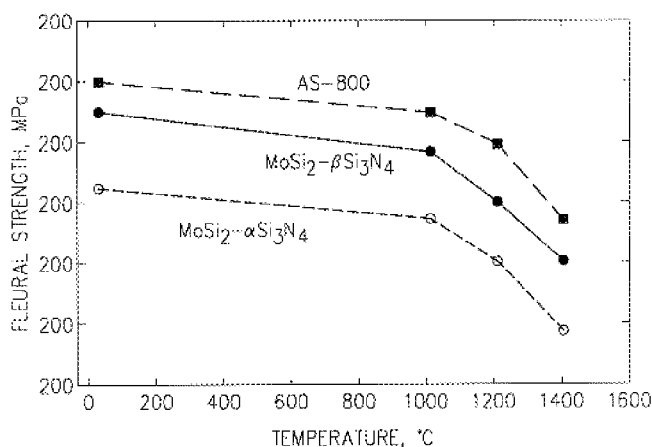
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Primary Examiner—Karl Group**(74) Attorney, Agent, or Firm—Pearne & Gordon LLP****(57) ABSTRACT**

A MoSi₂ pest resistant material includes in-situ grown β -Si₃N₄ whiskers. In addition to excellent pest resistance, the material provides a lower coefficient of thermal expansion for better match with continuous reinforcing fibers such as SiC fibers. A two stage heating and pressing production technique enables lower temperature processing with substantially full densification.

11 Claims, 2 Drawing Sheets

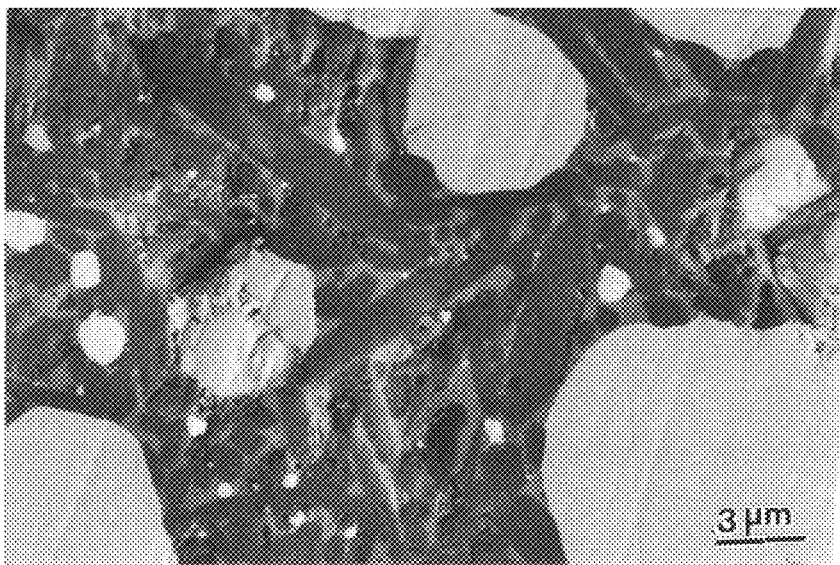


FIG. 1

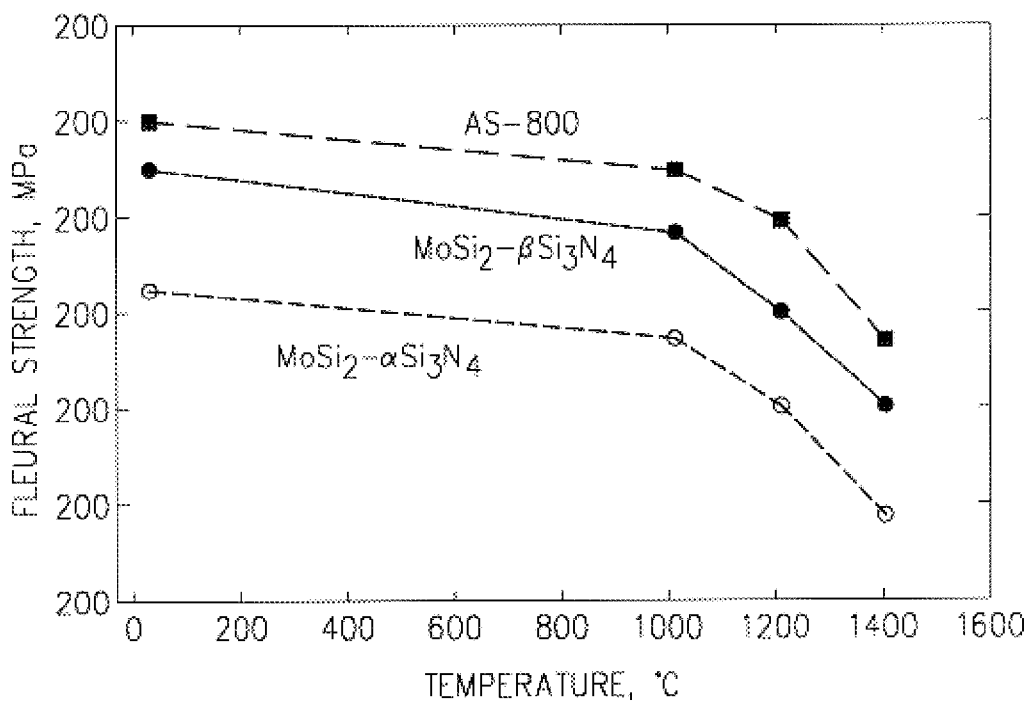


FIG. 2

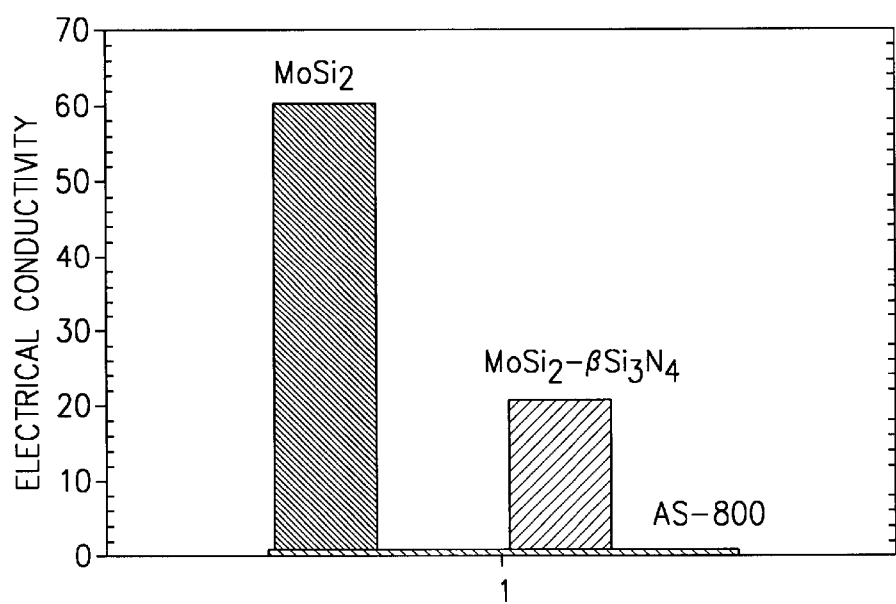


FIG. 3

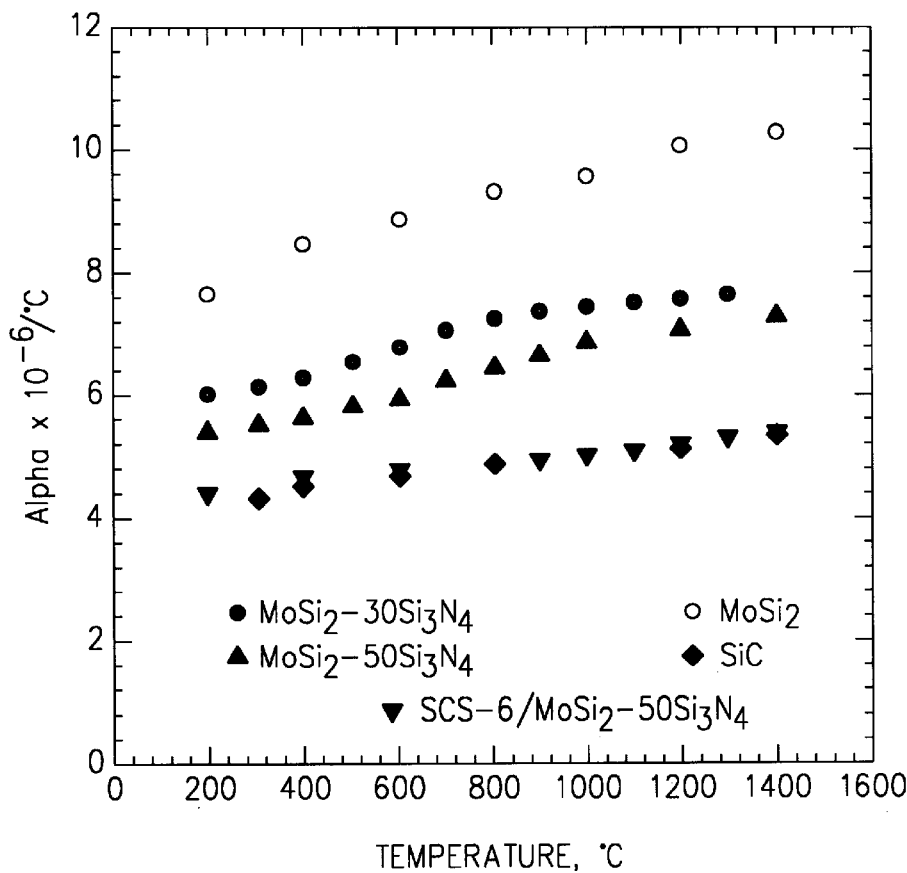


FIG. 4

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PEST RESISTANT MoSi_2 -BASED MATERIALS CONTAINING IN-SITU GROWN $\beta\text{-Si}_3\text{N}_4$ WHISKERS

This invention was made with Government support under Contract No. NCC-3-637 by NASA. The Government has certain rights to the invention.

BACKGROUND OF THE INVENTION

The present invention relates to intermetallic materials based on MoSi_2 , intermetallic matrix composites and methods of making the same. More particularly, the invention is directed to a MoSi_2 based material having an engineered micro-structure provided through the use of in-situ reinforcement whiskers.

MoSi_2 is an attractive intermetallic for structural applications due to its excellent high-temperature oxidation resistance, low density and high thermal conductivity. However, it is brittle at low temperatures, weak at high temperatures and suffers from accelerated oxidation at intermediate temperatures. The accelerated oxidation of MoSi_2 at intermediate temperatures causes the material to disintegrate into powder, a phenomenon known as pesting.

Pesting is a general term describing the catastrophic oxidation of intermetallic materials at intermediate temperatures. The accelerated oxidation leads to the disintegration of the material and component failure. For MoSi_2 the temperature at which pesting is most pronounced is approximately 500°C . It has been observed that at 500°C . bulk (i.e., non-composite) MoSi_2 , as well as, composites of MoSi_2 with alumina and aluminum nitride also suffer total disintegration within relatively short time periods, e.g. 100 hours.

The pested samples yield powdery products consisting of MoO_3 whiskers, SiO_2 clusters, and residual MoSi_2 . The MoO_3 whiskers exhibited protruding characteristics and were concentrated at the grain boundaries and cracks. The pesting phenomenon in MoSi_2 has been concluded to be the result of the formation of voluminous molybdenum oxides in microcracks. While not wanting to be bound by theory, the accelerated oxidation apparently involves the simultaneous formation of MoO_3 and SiO_2 in amounts essentially determined by the Mo and Si concentrations in the intermetallic.

The addition of about 30 to 50 volume percent of Si_3N_4 particulate to MoSi_2 reduced the pesting by forming a protective oxide scale as disclosed in assignee's related U.S. Pat. No. 5,429,997, the teachings of which are hereby incorporated by reference. In addition, improvements in room temperature fracture toughness, reductions in the 1200°C . compressive creep rates and lowered coefficient of thermal expansion were attained. Additional improvements in toughness and elevated temperature strength were achieved by reinforcing the $\text{MoSi}_2\text{-Si}_3\text{N}_4$ matrix with about 30 volume percent of silicon carbide continuous fibers. The use of fiber reinforcement is not entirely satisfactory due to the high costs of the present state-of-the-art techniques for making fiber reinforced, composites.

A further difficulty with the use of fiber reinforcement is the coefficient of thermal expansion mismatch between MoSi_2 and most potential reinforcing materials. MoSi_2 has a relatively high coefficient of thermal expansion as compared to most potential reinforcing materials such as silicon carbide fibers. The coefficient of thermal expansion mismatch between the fiber and the matrix material tends to result in matrix cracking during fabrication and severe matrix cracking during thermal cycling which in turn results

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in component failure. Possible reinforcing fibers include high strength ceramic fibers such as silicon carbide, single crystal alumina, and ductile, high strength molybdenum and tungsten alloy fibers. Ductile niobium fibers have shown improvements in low temperatures strength and toughness, but a severe reaction between the fiber and MoSi_2 limits its use and, in any case, it does not provide improved high-temperature characteristics. The addition of silicon carbide whiskers has yielded improvements in room temperature toughness, but pesting and coefficient of thermal expansion mismatch continue to be problems.

SUMMARY OF THE INVENTION

It has now been discovered that a MoSi_2 based material may be provided with an engineered micro-structure through processing and composition control. In-situ reinforcement of whisker type $\beta\text{-Si}_3\text{N}_4$ grains in a MoSi_2 matrix offers a unique combination of attributes. The in-situ reinforcement is believed to provide a more tortuous crack path with elongated grains or whiskers which lead to crack bridging and deflection resulting in very high fracture toughness.

The invention contemplates a new MoSi_2 based alloy composition which exhibits excellent pest resistance at low temperatures (400 to 600°C .), good coefficient of thermal expansion match with potential fiber reinforcement, excellent oxidation resistance at elevated temperatures and high fracture toughness enabling its use as a monolithic material. Accordingly, a MoSi_2 -based matrix contains a high-volume fraction of randomly oriented in-situ grown long whisker type grains of $\beta\text{-Si}_3\text{N}_4$ in the MoSi_2 matrix. The matrix is characterized in part by a toughened micro-structure, lower density, lower coefficient of thermal expansion, excellent resistance to pest attack, and it is much stronger than the binary MoSi_2 material.

The invention also contemplates processing conditions to achieve fully dense alloys with engineered microstructure through the use of sintering aids to grow the long whiskers of $\beta\text{-Si}_3\text{N}_4$ in the matrix. During processing, high-temperature and pressure conditions are used to convert the $\alpha\text{-Si}_3\text{N}_4$ particles to randomly oriented $\beta\text{-Si}_3\text{N}_4$ long whiskers. Suitable sintering aids include rare earth oxides.

It is presently believed that the improved pesting is related to the formation of more protective silicon oxy nitride, Si_2ON_2 , and/or mullite/ SiO_2 oxide scales that suppress the formation of non-protective MoO_3 . The invention also contemplates forming an outer protective layer of $\text{Al}_2\text{O}_3\text{-SiO}_2$ followed by an inner layer of SiO_2 for better oxidation resistance in reducing or low partial pressure oxygen atmospheres.

The invention also contemplates the use of the $\text{MoSi}_2\text{-}\beta\text{Si}_3\text{N}_4$ as a matrix in a ceramic fiber reinforced composite to achieve high specific strength, high first matrix cracking stressed and toughness without exhibiting any pesting or cracking during long-term thermal cycling at high and low temperatures. Silicon carbide fibers comprise a preferred reinforcing fiber.

According to a first preferred composition of the invention, there's provided MoSi_2 based matrix materials containing at least about 20 percent by volume $\beta\text{-Si}_3\text{N}_4$ whisker type grains based on the combined volume of the MoSi_2 and the $\beta\text{-Si}_3\text{N}_4$. More preferably, the composition of the invention comprises from about 30 to about 50 percent by volume $\beta\text{-Si}_3\text{N}_4$ based on the combined volume of the MoSi_2 and $\beta\text{-Si}_3\text{N}_4$.

The achievement of the whisker type $\beta\text{-Si}_3\text{N}_4$ grains is enhanced by the use of rare earth oxide sintering aids. The

rare earth oxides are nano sized. Preferred rare earth oxides include Y_2O_3 and Al_2O_3 . The sintering aids are used in amounts ranging from 2 to 6 percent by weight based on the combined weight of the $MoSi_2$ and $\beta-Si_3N_4$.

A preferred fiber reinforced composite comprises the above noted $MoSi_2$ - $\beta-Si_3N_4$ composition as a matrix material and ceramic reinforcing fiber. The reinforcing fiber is interspersed with the matrix material. The matrix material comprises at least about 50 percent, and more preferably about 70 percent by volume of the composite based on the combined volume of the matrix material and the $\beta-Si_3N_4$ reinforcing fiber. In more preferred arrangements, the reinforcing fiber is a silicon carbide fiber, and it is present in the matrix in an amount of about 30 percent by volume based on the combined volume of the matrix and the reinforcing fiber.

In accordance with the method of the present invention and preferred processing, mixtures of $MoSi_2$ and Si_3N_4 are blended and milled to micrometer particle size with the prior addition of sintering aids. The mixtures are formed into thin sheets or plates using vacuum hot pressing to achieve a relatively high green density. This first stage is followed by hot isostatic pressing to achieve full density as well as growth of whisker type grains of $\beta-Si_3N_4$. This two stage processing with the use of sintering aids enables reduction of the maximum heating temperature without reduction of the final level of densification.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a SEM-BS image showing the long whisker type $\beta-Si_3N_4$ grains randomly distributed in a $MoSi_2$ matrix;

FIG. 2 is a plot showing the flexural strength at various temperatures for $MoSi_2$ - $\beta-Si_3N_4$ and AS-800;

FIG. 3 is a graphical comparison of the electrical conductivity of various materials; and

FIG. 4 is a plot showing the reduced coefficient of thermal expansion for $MoSi_2$ compounds with in-situ $\beta-Si_3N_4$ whiskers.

DETAILED DESCRIPTION OF THE INVENTION

The in-situ reinforced $MoSi_2$ - $\beta-Si_3N_4$ yields a highly developed microstructure characterized by desirable physical properties. The in-situ reinforced materials have a lower density (4.5 g/cc) than nickel or cobalt based superalloys (about 8.5 g/cc). In addition, higher fracture toughness (about 20 MPa(m)^{0.5}) and impact resistance at room and operating temperatures as compared with SiC/SiC. The in-situ reinforced alloys also provide improved damage tolerance, reliability and creep resistance as compared with SiC/SiC. Also, higher thermal and electrical conductivities are achieved than with SiC/SiC. As noted above, the in-situ reinforced materials also enable low cost EDM and laser machining. It should be appreciated that the SiC/SiC materials are more costly since they employ fibers and coatings.

In accordance with the invention, mixtures of $MoSi_2$ and Si_3N_4 are blended and milled to obtain an average particle size of less than about two micrometers in diameter. The mixtures are then consolidated into thin sheets or plates using vacuum hot pressing to achieve a relatively high density, e.g., 90 percent green density. Full density as well as growth of whisker type grains of $\beta-Si_3N_4$ are achieved with hot isostatic pressing. In this manner, the $\alpha-Si_3N_4$ particles are transformed into $\beta-Si_3N_4$ as randomly oriented long whiskers that are well dispersed in the $MoSi_2$ matrix.

EXAMPLE 1

$MoSi_2$ based alloys consisting essentially in amounts by volume percent of about 30 to 50 percent Si_3N_4 having a

particle size of one to two microns were prepared in the following manner. The Si_3N_4 obtained from UBE Inc. was ground in a Union Process Model 1-S attritor mill for about eight hours using WC grinding media. The grinding media had a diameter of about six mm, and a ball to powder ratio of 20 was used to reduce about 95 percent of the particles to a size of less than two microns.

$MoSi_2$ powder having at least 98.5 percent purity and a -325 mesh size was obtained from Johnson Matthey Inc., (Aesar Inc.). The $MoSi_2$ powder was combined with the ground Si_3N_4 and about 2-6% by weight sintering aids. The sintering aids were nano size rare earth oxides such as Y_2O_3 and Al_2O_3 obtained from Nanotek Inc.

Three batches of about 530 grams each were prepared as described above, and combined in a SiC jar mill containing about 1500 grams of silicon carbide grinding media in the form of six mm diameter balls. The combined batches were milled for about 24 hours.

The combined batches were then further milled in the Union Process Model Research 1-S attritor with an impeller rotation speed out 450 rpm for eight hours using six mm diameter WC grinding media. The ball to powder ratio was 20:1. The outer jacket of the attritor was cooled with flowing liquid nitrogen to promote efficient grinding. After eight hours of milling, the powder was separated anaerobically from the grinding media in a glovebox containing an argon atmosphere. The resulting powder mixture had an average mean particle size of 1.25 ± 0.71 micrometers at 99 percent confidence.

The powder mixture was consolidated into a 12 cm long by 5 cm wide by 0.3 cm thick plate by vacuum hot pressing at 1600° C. and 128 MPa or 1800° C. and 84 MPa for four hours to achieve more than 90 percent green density. The hot pressed plate was enclosed in a tantalum hot isostatic press (HIP) canister together with a silicon carbide back-up plate. The HIP canister was sealed using electron beam welding. Further consolidation of the hot pressed plate was achieved by hot isostatic pressing between 1800-1900° C. and 300 MPa for two hours. During hot isostatic pressing, full densification as well as growth of whisker type grains of $\beta-Si_3N_4$ were achieved. The use on the sintering aids and the two-step consolidation process enabled the use of lower temperatures then could be used if hot pressing were done alone for purposes of growing $\beta-Si_3N_4$ grains. (e.g. if hot pressing alone were used, the required temperature would be in the range of 2000-2100° C. at 126 MPa for four hours.) This resulted in fully dense and $\beta-Si_3N_4$ grained microstructure as shown in FIG. 1. The $\alpha-Si_3N_4$ particles are transformed into $\beta-Si_3N_4$ as randomly oriented long whiskers that are well dispersed in the $MoSi_2$ matrix. The $\beta-Si_3N_4$ whiskers appear to be quite stable, with very little or no reaction with the $MoSi_2$ even at 1900° C. In some isolated areas the Mo_5Si_3 phase was detected. This is believed to be due to the lack of stoichiometry in commercially available $MoSi_2$.

The fracture toughness of the materials in accordance with Example 1 was measured at room temperature by preparing ASTM chevron notched bend specimens. For purposes of testing, a second duplicate batch of materials was prepared and the samples are referred to below as being of batch 1 or batch 2. The fracture testing was done at room temperature using an Instron test machine fitted with a four point bend fixture.

From the load displacement data and specimen dimensions, the valid K_{Ic} was calculated using a slice finite element model. The slice model is based on the relationship:

$$K_{Ic}=[P(S_1-S_2)Y^*]/(W^3/2)$$

Where K_{Ic} is the fracture toughness in MPa(m)^{0.5},
P is the load at break in MPa,
 S_1 and S_2 define the gripped sample span,
Y is a sample geometry constant,
B is the sample thickness in mm,
W is the sample width in mm,

TABLE 1

Sample	B (mm)	W (mm)	α_o	A_1	Y*	P (N)	K_{Ic} (MPa (m) ⁻⁵)
Batch I							
MS-1	3	6	1.2	4.8	3.28	194.9	14.02
MS-2	3	6	1.2	4.8	3.28	208.9	14.96
MS-3	3	6	1.2	4.8	3.28	273.4	20.2
Batch II							
MS-4	3	6	1.2	4.8	3.28	250.4	18.0
MS-5	3	6	1.2	4.8	3.2	262	18.9
MS-6	3	6	1.2	4.8	3.28	208.5	16.0
Average							17.0

α_o , A_1 and Y* are constants based on sample geometry
MATERIAL ID: MoSi₂-β50Si₃N₄
TEST TEMP.: ROOM TEMP
CROSS HEAD SPEED: 8.5 × 10⁻⁵ s⁻¹
POISSON'S RATIO: 0.32

The average K_{Ic} of this material was about 17 MPa(m)^{0.5}. The room temperature fracture toughness of MoSi₂-Si₃N₄ without the whiskers of β-Si₃N₄ was about 5.0 MPa(m)^{0.5}. Accordingly, the β-Si₃N₄ whiskers improved the fracture toughness by more than a factor of three as compared with the Si₃N₄ particulate in MoSi₂.

The in-situ Si₃N₄ toughened MoSi₂ has a higher fracture toughness than commercially available in-situ toughened Si₃N₄. For example, AS-800 has a fracture toughness of about 8.5 MPa(m)^{0.5} and NKK has a fracture toughness of about 10 MPa(m)^{0.5}. The higher fracture toughness of MoSi₂-β-Si₃N₄ as compared to in-situ toughened Si₃N₄ is believed to be derived from the combined effects of efficient crack bridging, grain pull-out (due to weak bonding with MoSi₂ matrix) of highly elongated Si₃N₄ grains and the larger grain size of MoSi₂. The primary toughening mechanisms such as crack bridging and grain pull-out lead to a rising crack growth resistance curve (R-curve behavior) as confirmed by the testing of this material using the indentation crack size, indentation-strength method, SEPB and chevron notched bend method as indicated by the data of Table 1. A consequence of this R-curve is that this material will have a higher Weibull modulus.

The flexural strength of the material of Example 1 was measured using ASTM standard specimens (3 mm thick by 6 mm wide by 50 mm long MOR bars) of MoSi₂-βSi₃N₄ at various temperatures between room temperature and 1400° C. in air. FIG. 2 shows the flexural strength of MoSi₂-βSi₃N₄, MoSi₂-αSi₃N₄ and AS-800 as a function of temperature. FIG. 2 clearly indicates that the strength of AS-800 is superior to MoSi₂-βSi₃N₄ at all temperatures. Also, the strength of MoSi₂-βSi₃N₄ is higher than MoSi₂-αSi₃N₄. As an intermetallic compound, the MoSi₂ offers significant potential for further improving the strength by solid solution alloying.

High-temperature cyclic oxidation test were carried out on rectangular coupons of MoSi₂-50βSi₃N₄ at 1000° and

1350° C. in air for about 100 cycles. Each cycle consisted of one hour heating followed by 0.3 hours of cooling. The material of example 1 exhibited a parabolic oxidation behavior with weight gain of only 0.03 and 0.4 mg/cm² at 1000° and 1350° C. respectively. These weight gain values are smaller than those obtained for AS-800 (0.06 and 0.63 at 1000° and 1350° C. respectively). The x-ray diffraction of the oxidized surface of MoSi₂-βSi₃N₄ indicated strong peaks of SiO₂, a protective scale.

The ability of a material to undergo electro-discharge machining (EDM), a widely accepted low-cost machining technique, is indicated by its electrical conductivity. Room temperature electrical conductivities of various MoSi₂ based materials and Si₃N₄ based materials were measured using MOR bars (6 mm wide by 3 mm thick by 50 mm long). As shown in FIG. 3, the electrical conductivity of MoSi₂-βSi₃N₄ based material is more than an order of magnitude higher than the conductivity of AS-800 materials, and EDM may be used with the former but not the latter.

Referring to FIG. 4, the coefficient of thermal expansion for MoSi₂ compounds reinforced with in-situ grown β-Si₃N₄ whiskers is compared with non-reinforced MoSi₂ and possible reinforcing fiber material such as SiC at various temperatures. As shown, the coefficient of thermal expansion is increasingly reduced for 30 and 50% volume percent β-Si₃N₄ whiskers as indicated by samples MoSi₂-30Si₃N₄ and MoSi₂-50Si₃N₄. In a further comparison, MoSi₂ reinforced with 50% by volume β-Si₃N₄ and 30% by volume SCS-6 silicon carbide fibers has a coefficient of thermal expansion very close to that of SiC. The reduction of the coefficient of thermal expansion in accordance with the invention thereby provides a better match with possible reinforcing fibers.

Many modifications and variations of the invention will be apparent to those skilled in the art in light of the foregoing detailed than disclosure. Therefore, within the scope of the appended claims, the invention can be practiced otherwise than as specifically shown and described.

What is claimed is:

1. A method of improving pest resistance of a molybdenum disilicide matrix comprising forming in situ whiskers of β-Si₃N₄ in said molybdenum disilicide matrix.
2. The method of claim 1, wherein said matrix comprises at least 20% by volume whiskers of β-Si₃N₄ based on the combined volume of said molybdenum disilicide and whiskers of β-Si₃N₄.
3. The method of claim 2, wherein said matrix further comprises ceramic reinforcing material.
4. A method of making a pest resistant composition comprising the steps of forming a mixture of:
 - 50 molybdenum disilicide with at least about 20% by volume α-Si₃N₄ based on the combined volumes of molybdenum disilicide and α-Si₃N₄, and heating said mixture to form in-situ grown long whisker grains of β-Si₃N₄.
5. The method of claim 4, including adding to said mixture 2 to 6% by weight of a sintering aid based on the weight of said molybdenum disilicide and α-Si₃N₄.
6. The method of claim 5, wherein said sintering aid comprise rare earth oxides.
7. The method of claim 5, including providing said molybdenum disilicide and α-Si₃N₄ with particle sizes of less than about 2 μm.
8. The method of claim 5, including pressing said mixture to form a monolithic element.
9. The method of claim 5, including adding ceramic reinforcing material to said mixture.
10. The method of claim 5, wherein the step of heating includes a first stage with vacuum hot pressing at a first

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temperature to achieve partial green densification of said composition and a second stage with hot isostatic pressing at a second temperature higher than said first temperature to achieve substantially full densification of said composition.

11. The method of claim 10, wherein said first stage 5 includes vacuum hot pressing at a pressure of about 128

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MPa and a temperature of from about 1600 to about 1800° C., and said second stage includes hot isostatic pressing a pressure of about 300 MPa and a temperature of from about 1800 to about 1900° C.

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